

Laboratory Studies of Processing of Carbonaceous Aerosols by Atmospheric Oxidants

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Objective:

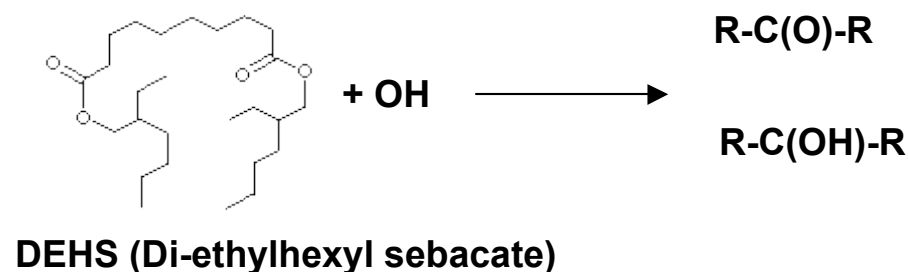
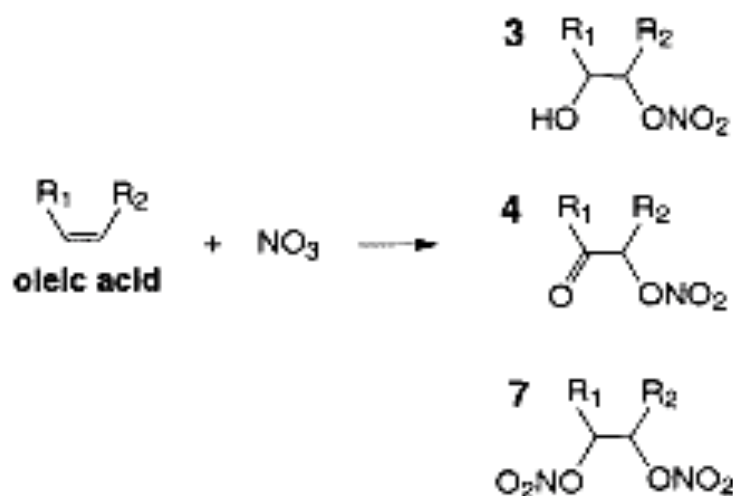
Examine the effect of **oxidative aging** on the **CCN activity** of model primary organic aerosol (POA):

oleic acid, linoleic acid, and DEHS

Methods:

- Oxidize aerosol particles in Riverside's 6 m³ smog chamber
- Use CCN counter to quantify changes in critical supersaturation (S_c) as a function of dry diameter (D_{dry}) between unoxidized and reacted particles
- Estimate impact of aging on particle lifetime against wet scavenging

POA Oxidation by OH and NO₃ Radicals



Oleic acid (one double bond)
Linoleic acid (two double bonds)

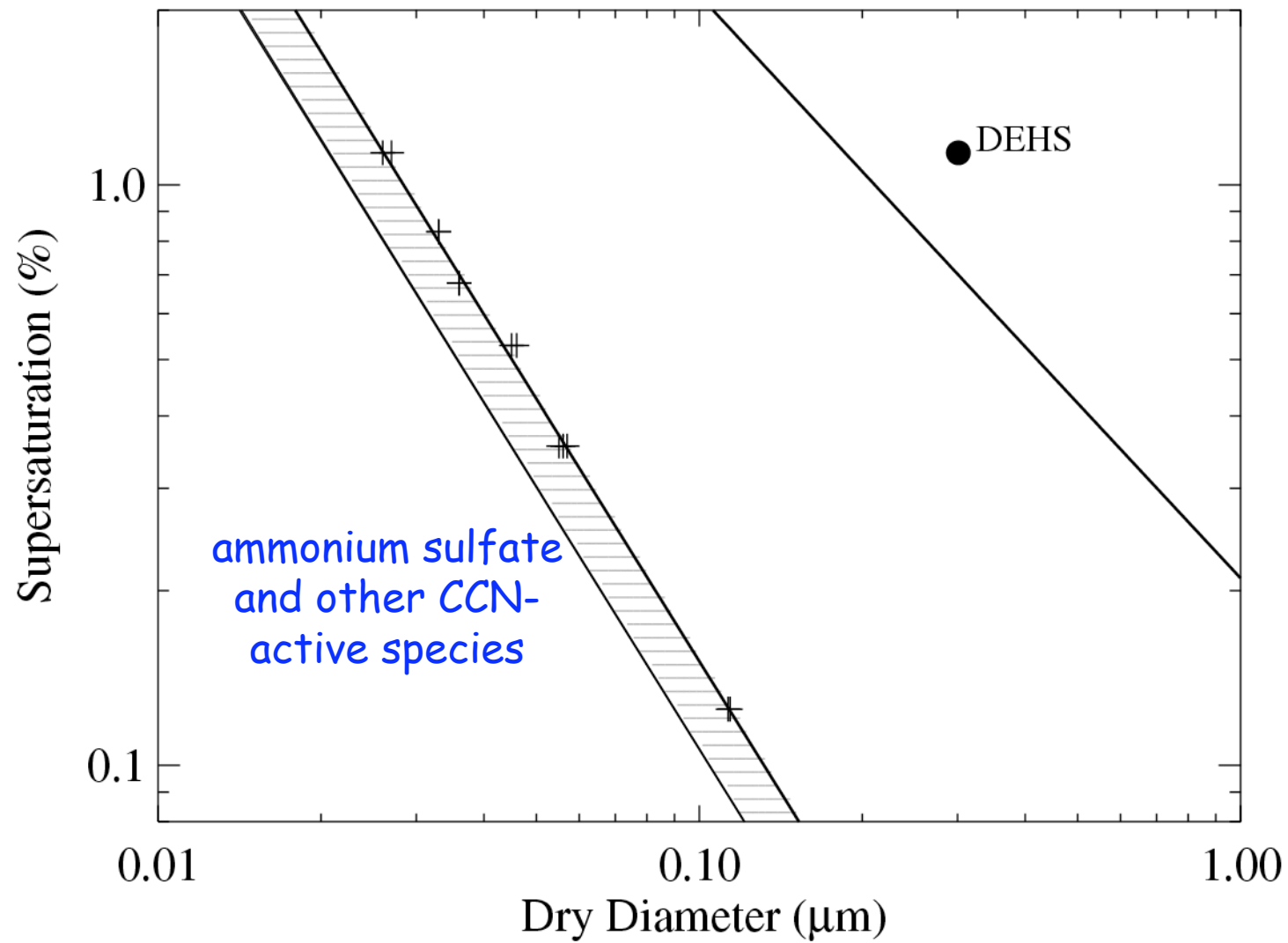
Full reaction simulates ~2-4 and ~8-14 days of chemical aging

Addition of ~1 functional group for every 200 carbon atoms

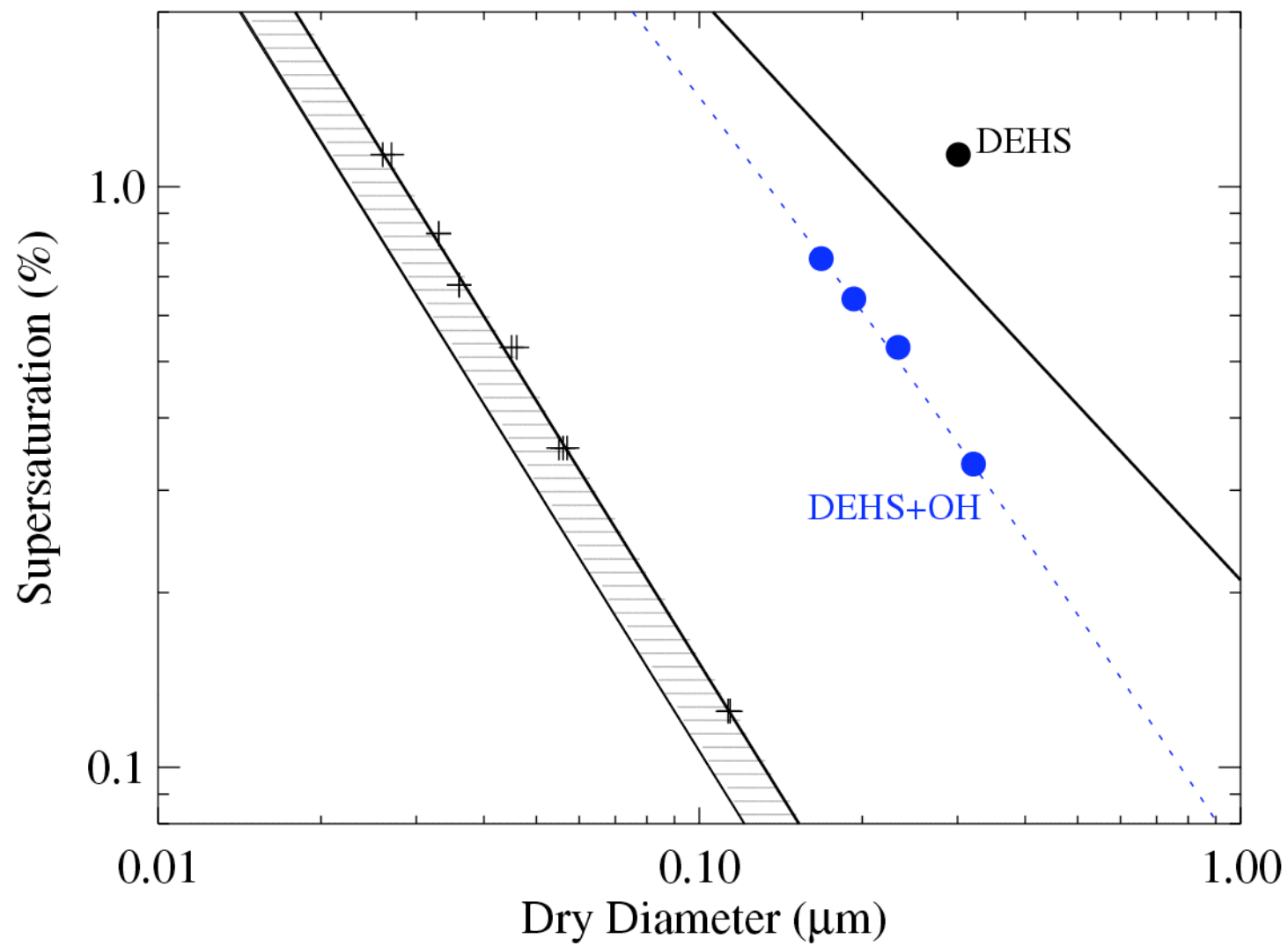
Similar to ~0.2 d of atmospheric processing.

It has been proposed that such aging makes these initially-hydrophobic materials **hygroscopic**
 (aged particles can then serve as CCN and are removed by precipitation)

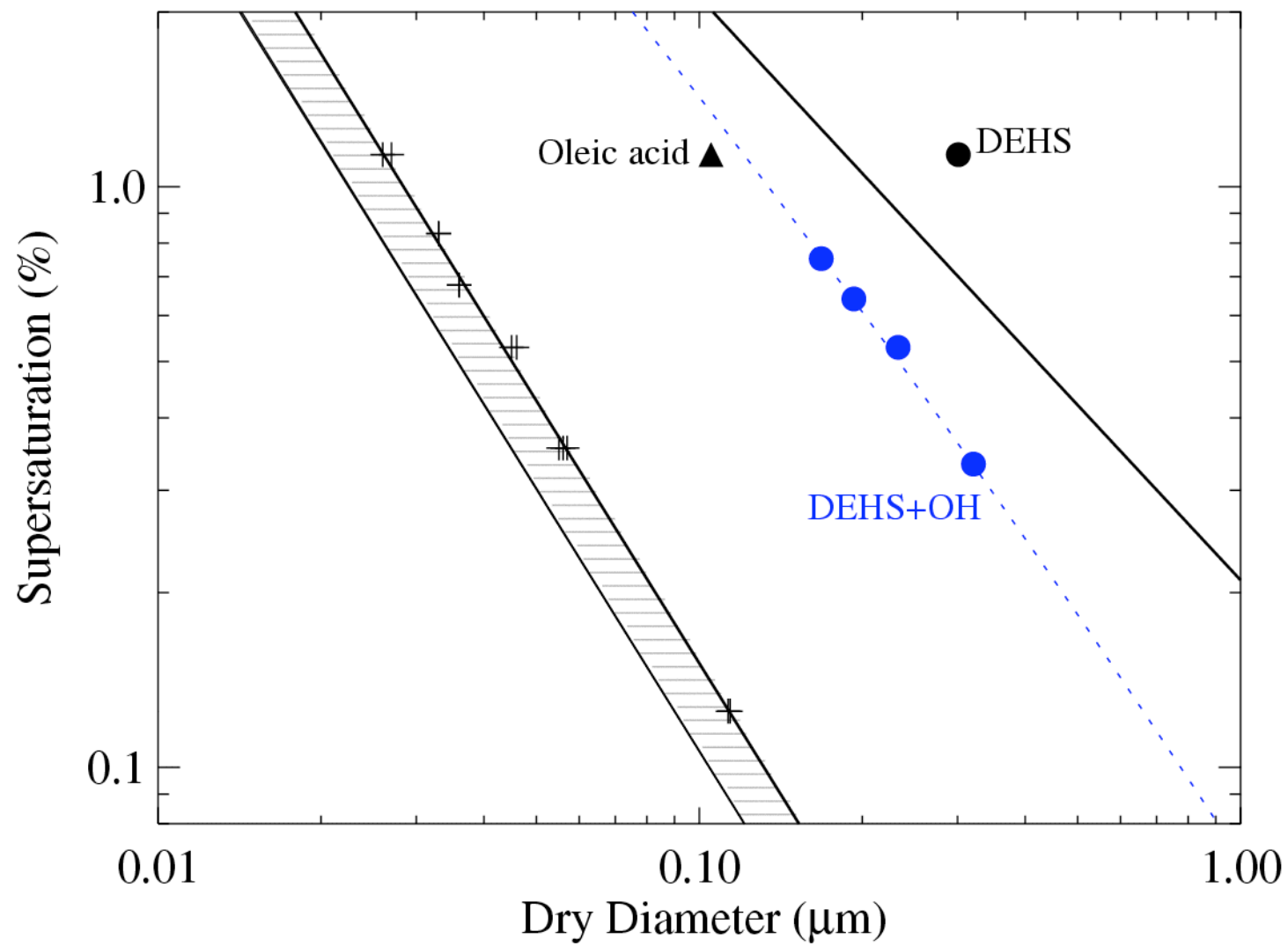
Chemical Aging of POA



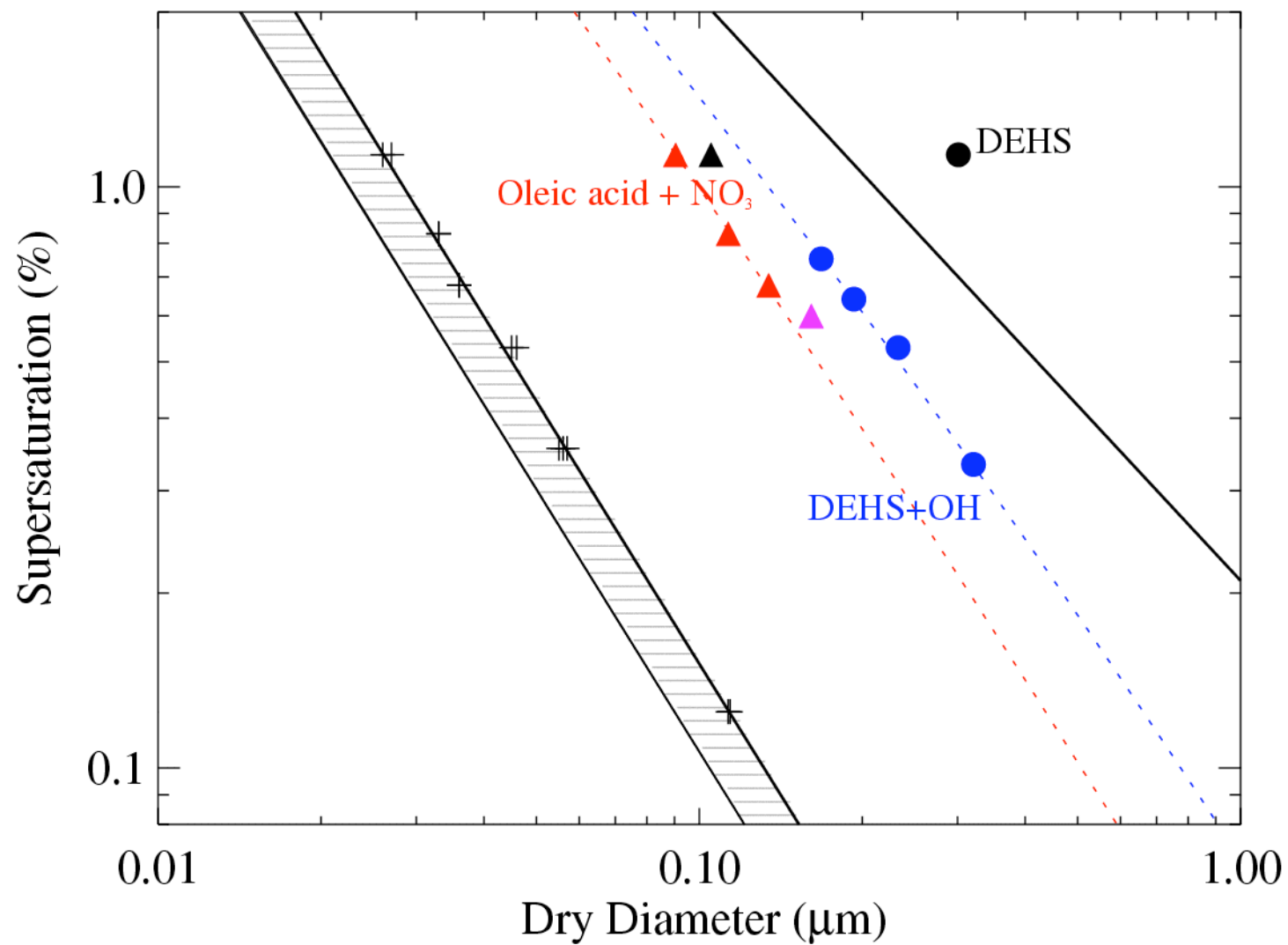
Chemical Aging of POA



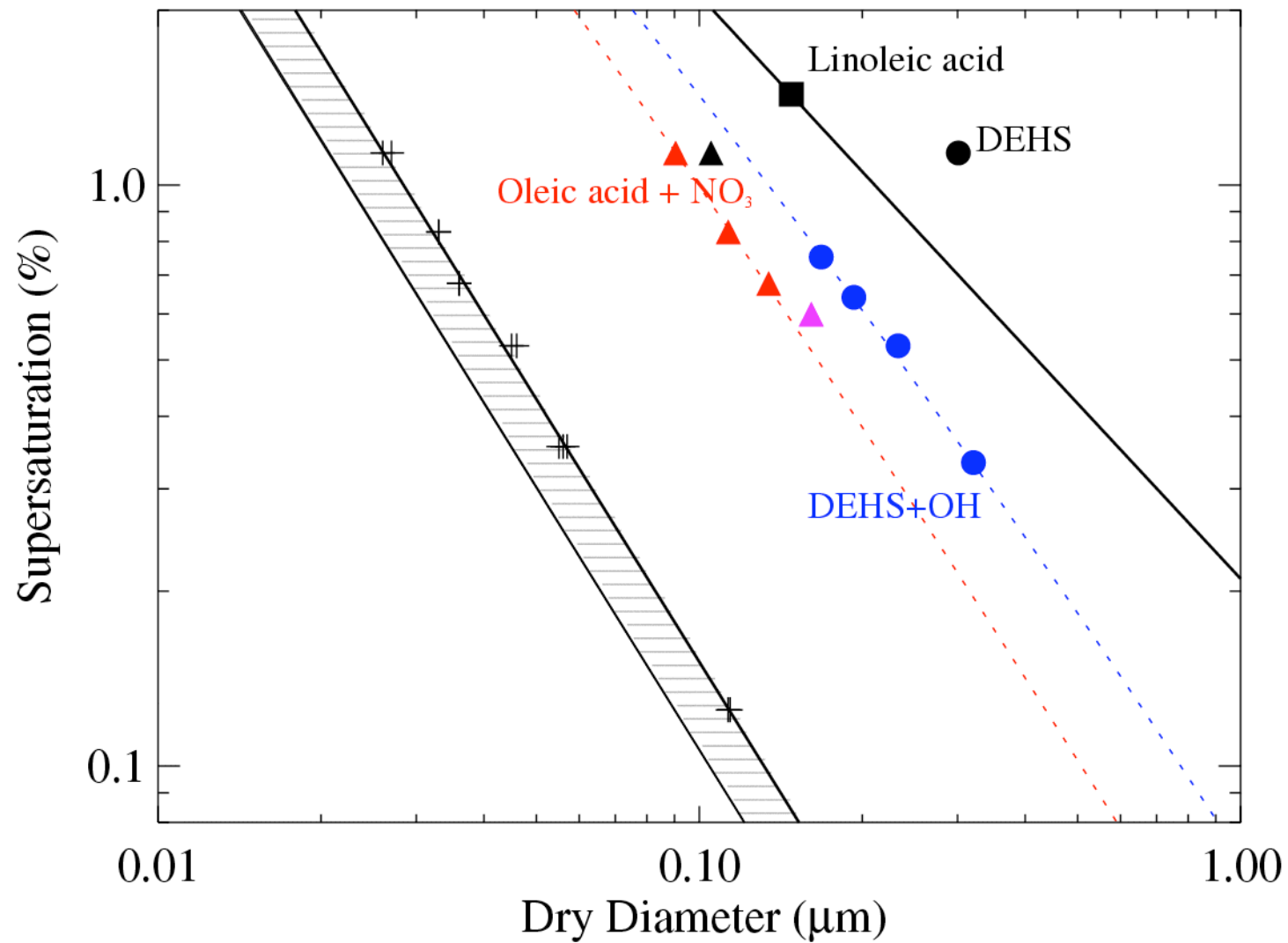
Chemical Aging of POA



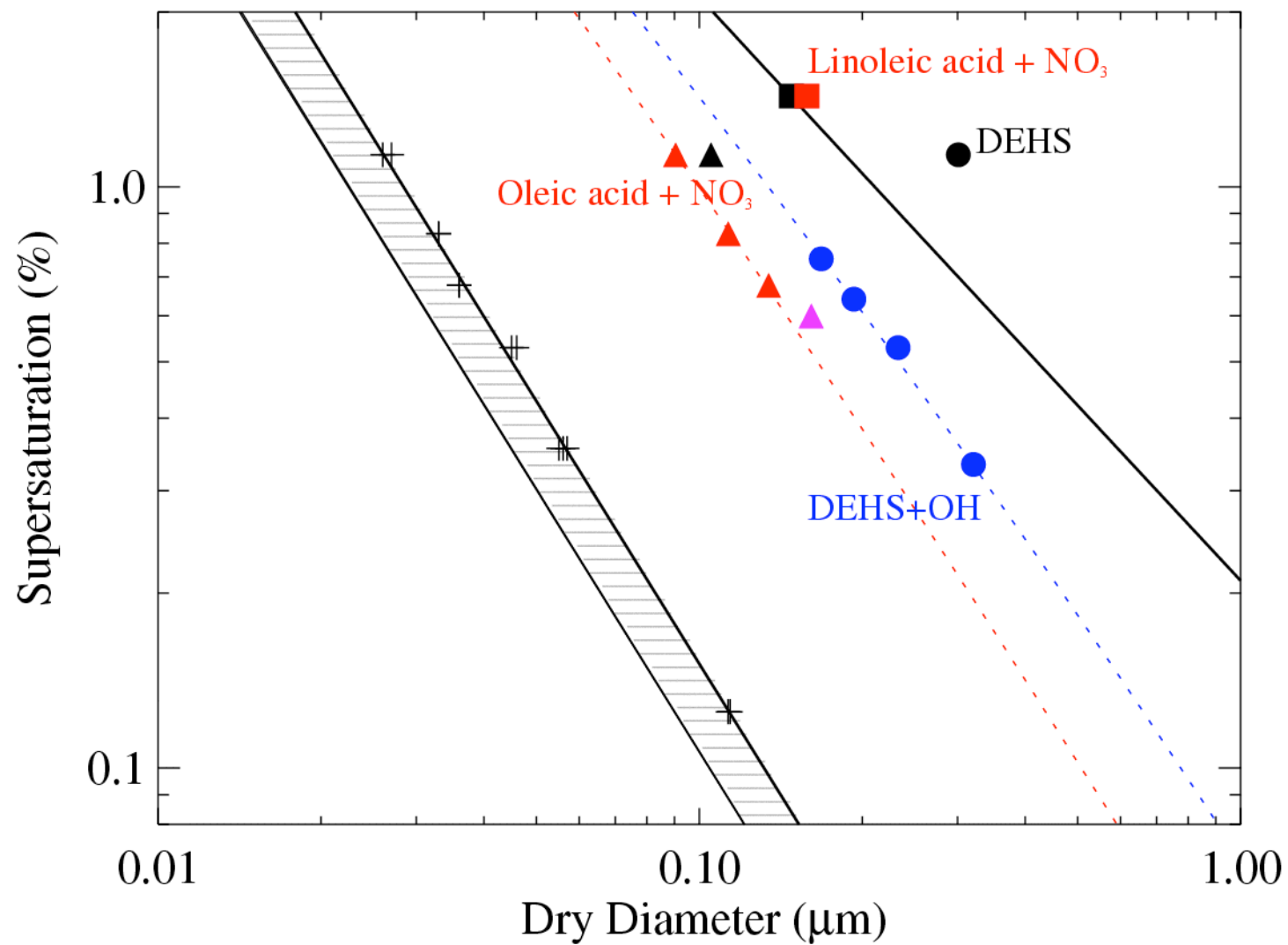
Chemical Aging of POA



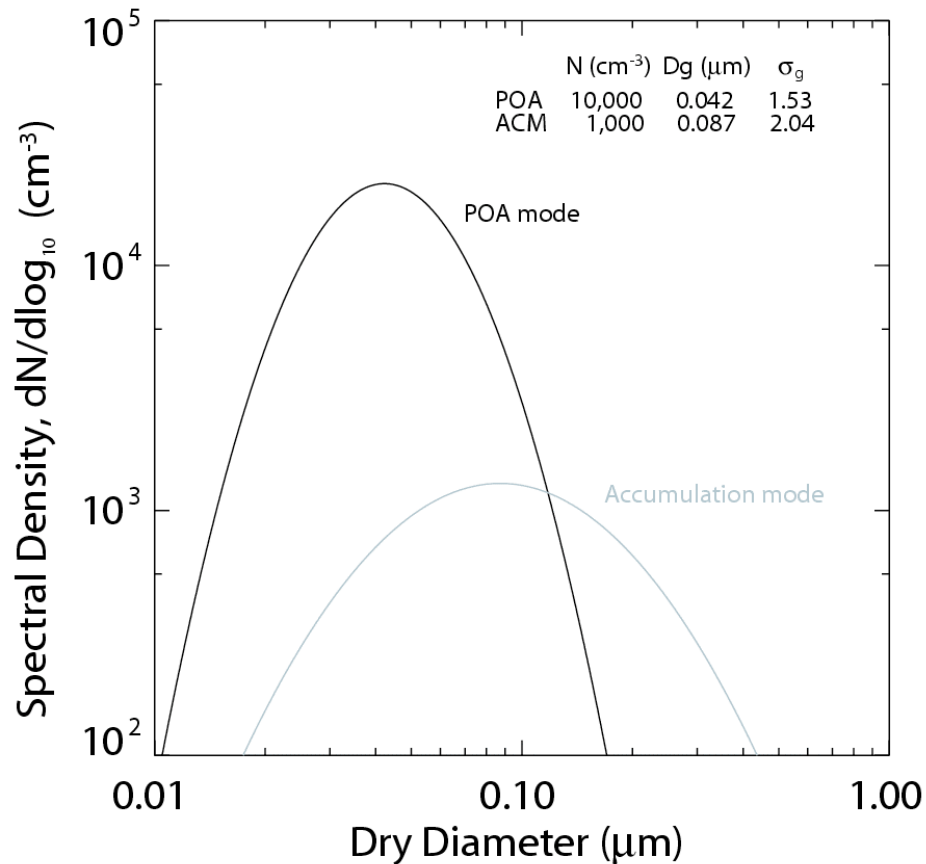
Chemical Aging of POA



Chemical Aging of POA



Scavenging of POA in Clouds



Does this POA, after ageing, become hygroscopic enough to act as CCN?

Run parcel model to find conditions for which 60% of POA mass (20% of N) is activated

Vary parameter space:

- Fix hygroscopicity of accumulation mode aerosol (activated first) to simulate mixed organic+sulfate aerosol, but vary the number concentrations
- Vary the CCN activity assigned to the POA (from very **non**-hygroscopic to very hygroscopic)
- Use 2 assumptions about N_{POA}
- Vary updrafts

Conclusions

- Increases in hygroscopicity of primary organic aerosols due to chemical aging (here, heterogeneous oxidation) should not affect their atmospheric lifetimes
- The increase in CCN activity is not enough to overcome the inhibiting effect of their small sizes
- Probably coagulation / condensation involving more-hydrophilic species control size / hygroscopicity increases and therefore lifetimes

Laboratory and Modeling Study of the Effect of Oxidative Aging on POA CCN Activity

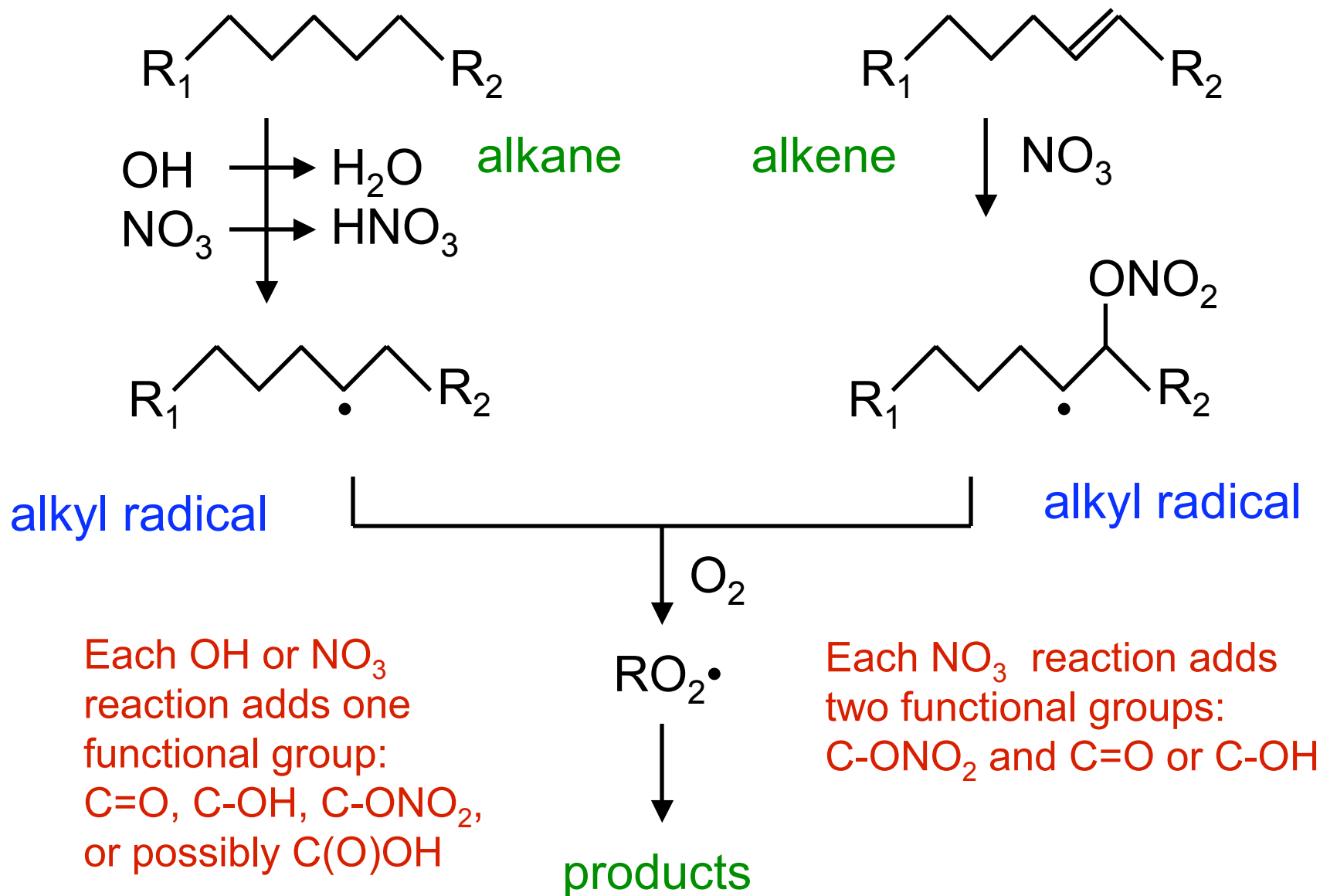
- Aerosol particles were oxidized in a 6 m³ smog chamber
DEHS (C₂₆ saturated diester) aerosol + OH radicals
Oleic acid and linoleic acid aerosols + NO₃ radicals
Oxidation adds C=O, C-OH, C-ONO₂ [C(O)OH already present on oleic and linoleic acids]
- Days of atmospheric oxidation by OH and NO₃ radicals required to achieve similar composition were calculated using kinetic theory, atmospheric [OH] and [NO₃], reactive uptake coefficients, and mean particle size

DEHS: addition of ~1 functional group for every 200 carbon atoms, similar to ~0.2 d of atmospheric processing.

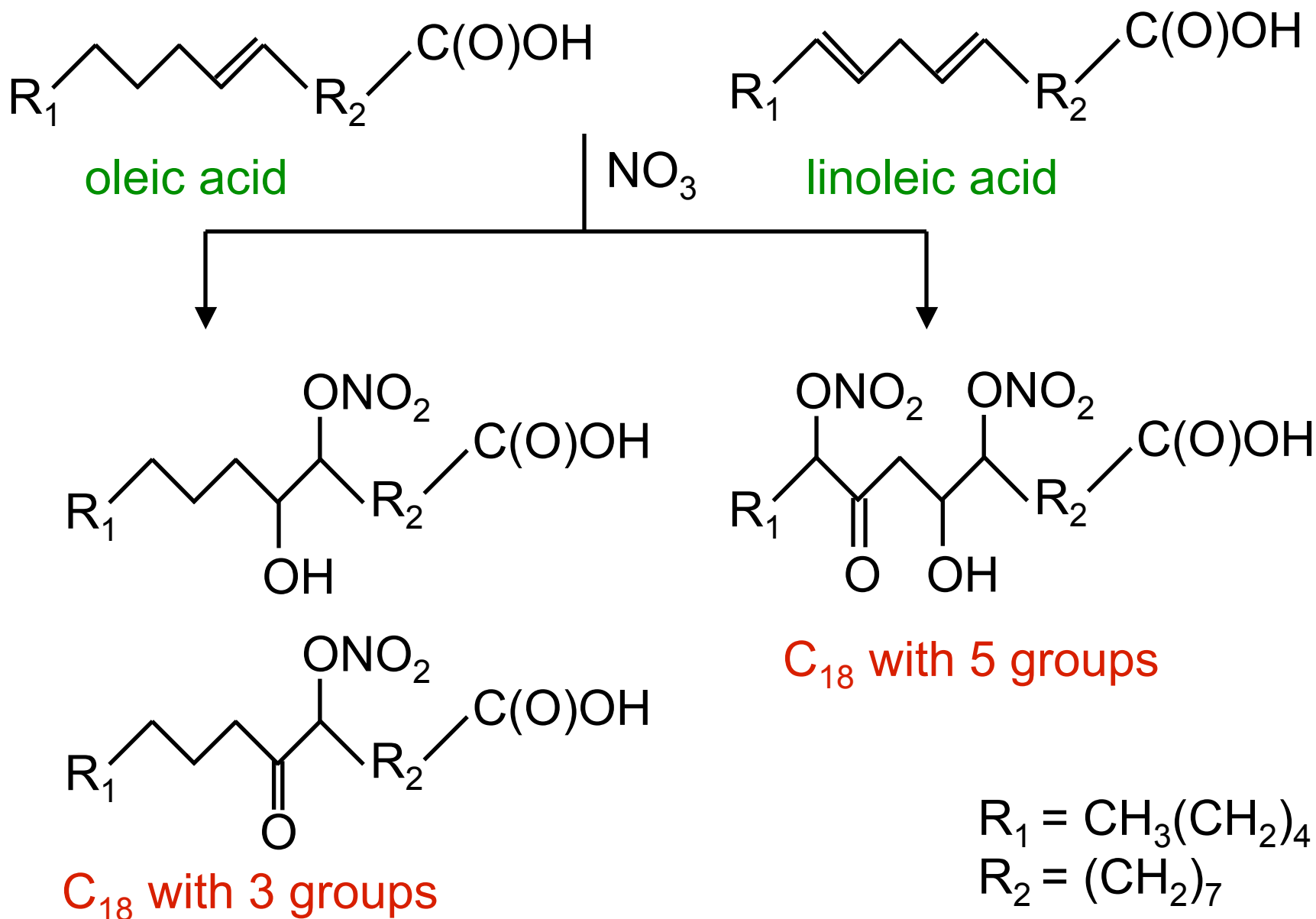
Oleic and linoleic acids:

- > 2 functional groups added to each oleic acid molecule
- > 4 functional groups to each linoleic acid molecule
- > Similar to ~8 and ~14 days of atmospheric processing under global average conditions and ~3 and ~5 days lower limit for high oxidants and maximum uptake coefficients

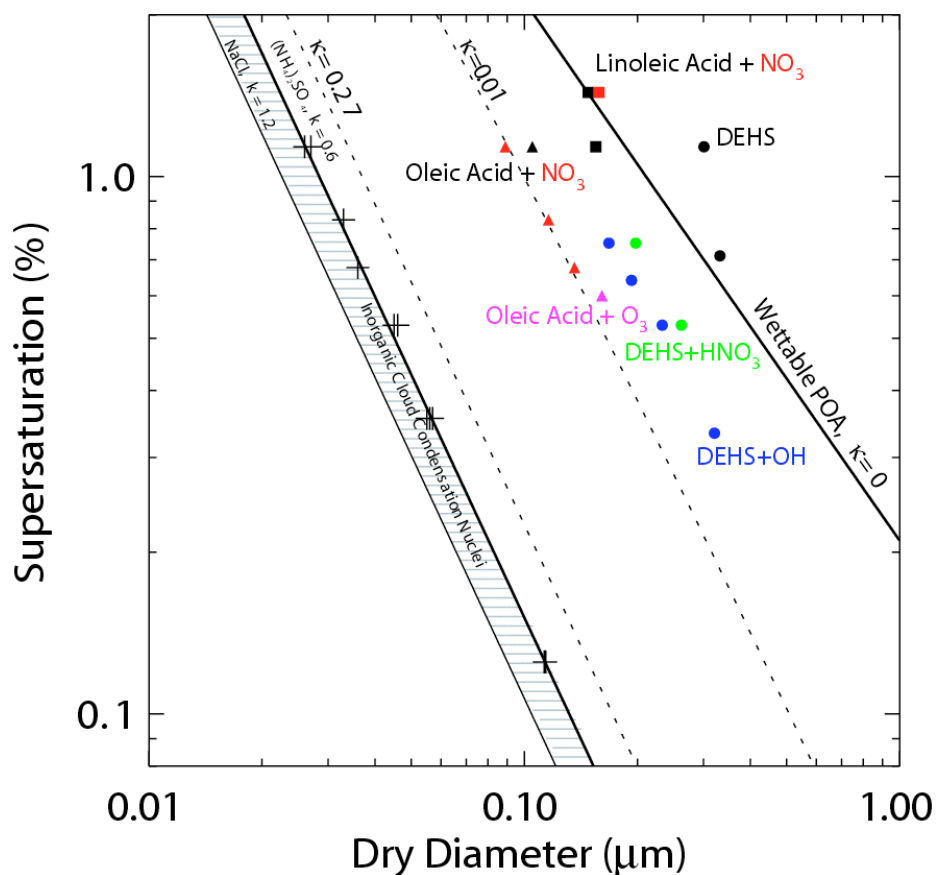
POA Oxidation by OH and NO₃ Radicals



Oleic and Linoleic Acid + NO₃ Reaction Products



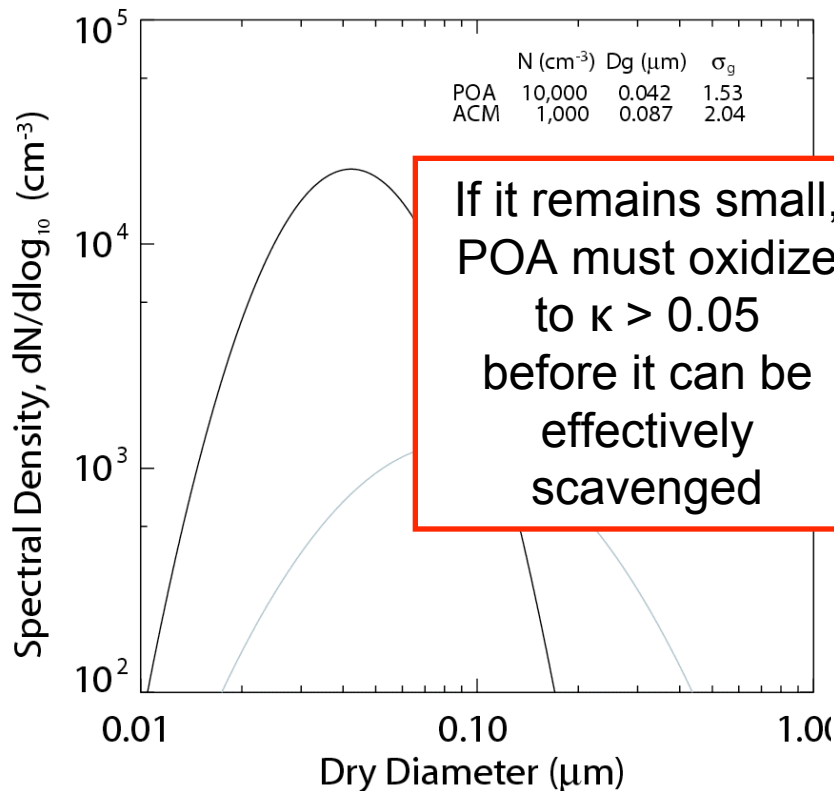
Chemical Aging of POA



- Linoleic acid: almost no change ($\kappa \sim 0.001$), even though fully reacted
- DEHS: measurable change from $\kappa \sim 0$ to $\kappa \sim 0.004$ (partially reacted)
- Oleic acid: fully reacted “limit” of $\kappa \sim 0.01$

Oleic acid + O_3 from Broekhuizen et al. (2004)

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